

REMARKS/ARGUMENTS

Claims 18-38 are pending in this application. By this Amendment, Applicants ADD Claims 35-38.

New Claim 35 is similar to Claim 24, including base Claim 18, but does not recite the feature of "with a degree of alignment of 0.95 or more" recited in Claim 18. New Claims 36, 37, and 38 correspond to Claims 19, 25, and 26, respectively.

On page 2 of the Office Action, the Examiner rejected Claim 18 under 35 U.S.C. § 103(a) as being unpatentable over Heeger et al. (U.S. 6,534,329).

Applicants respectfully traverse this rejection of Claim 18.

Applicants' Claim 18 recites:

An organic EL light emitting device comprising an organic EL light emitting layer and an electrode for applying a voltage to the organic EL light emitting layer, wherein the organic EL light emitting layer includes a **hyperbranched polymer layer having hyperbranched macromolecules uniaxially aligned with a degree of alignment of 0.95 or more** and emits polarized light. (emphasis added)

In Section No. 2 on page 2 of the outstanding Office Action, the Examiner noted that Heeger et al. teaches the use of poly(2-methoxy,5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) as conjugated polymers. The Examiner alleged that MEH-PPV teaches the feature of "a hyperbranched polymer layer having hyperbranched macromolecules" as recited in Claim 18. The Examiner admitted that Heeger et al. fails to teach or suggest the feature of "a hyperbranched polymer layer having hyperbranched macromolecules [that are] uniaxially aligned with a degree of alignment of 0.95 or more" as recited in Claim 18. However, the Examiner alleged that it would have been obvious to modify Heeger et al. such that the MEH-PPV polymers are uniaxially aligned with a degree of alignment of 0.95 or more in order to have the device of Heeger et al. emit polarized light.

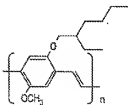
Applicants respectfully disagree.

First, Applicants respectfully submit that Heeger et al. fails to teach or suggest a hyperbranched polymer layer having hyperbranched macromolecules because Heeger et al. fails to teach or suggest a dendrimer structural unit or a hyperbranched polymer

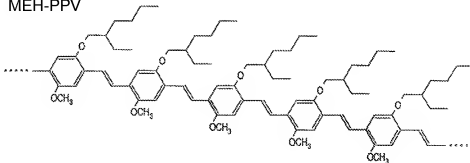
structural unit. The paragraph bridging pages 11 and 12 of the present Specification states, "[H]yperbranched macromolecule as used herein refers to a macromolecule that has at least one hyperbranched structural unit having a branched structure of an arbitrary shape. Herein, the 'hyperbranched structural unit' is defined to include a dendrimer structural unit [or] a hyperbranched polymer structural unit as diagrammatically illustrated in FIG. 1."

Applicants acknowledge that the present Specification teaches that polyphenylene vinylene (PPV) can be used as part of a dendrimer structural unit, for example, in the paragraph bridging pages 15 and 16 of the present Specification, which states, "[T]he dendron may be of a polymer structure such as ... a conjugated polymer structure such as ... polyphenylene vinylene [(PPV)]... ." However, the present Specification requires that, for example, the PPV dendrons be arranged in the specific pattern of a dendrimer structural unit shown, for example, in Applicants' Fig. 3. Heeger et al. is clearly silent on MEH-PPV being a dendron or being part of a dendrimer structural unit. As shown in the figure below, MEH-PPV is a conventional linear polymer.

MEH-PPV



MEH-PPV



Further, Applicants have attached Zhang et al., "A new hyperbranched polymer with polar chromophores for nonlinear optics," POLYMER, vol. 38, no. 12, 1997, pp. 2893-97 and Miller et al., "Electrically Conducting Dendrimers," J. Am. Chem. Soc., vol. 119, 1997, pp. 1005-10 that further explain and describe the structure and arrangement of hyperbranched polymers. Hawker et al., "Preparation Of Polymers With Controlled Molecular Architecture. A New Convergent Approach To Dendritic Macromolecules," J. Am. Chem. Soc., vol. 112, no. 21, 1990, pp. 7638-7647, which was cited in the IDS filed July 2, 2004, also explains and describes the structure and arrangement of hyperbranched polymers.

Thus, Applicants respectfully submit that Heeger et al. fails to teach or suggest the feature of "a hyperbranched polymer layer having hyperbranched macromolecules" as recited in Claim 18.

Second, Applicants respectfully submit that the Examiner has failed to provide proper motivation for modifying Heeger et al. to include "a hyperbranched polymer layer having hyperbranched macromolecules [that are] uniaxially aligned with a degree of alignment of 0.95 or more" as recited in Claim 18 because the Examiner has failed to provide any evidence that the prior art recognized that the degree of alignment of 0.95 or more is achievable or is desirable in hyperbranched macromolecules.

Instead of basing the conclusion of obviousness based upon Heeger et al. on actual teachings or suggestions of the prior art and the knowledge of one of ordinary skill in the art at the time the invention was made, the Examiner has improperly used Applicants' own invention as a guide. It is impermissible to use the claimed invention as an instruction manual or 'template' to piece together the teachings of the prior art so that the claimed invention is rendered obvious. The Federal Circuit has previously stated that one cannot use hindsight reconstruction to pick and choose among isolated disclosures in the prior art to deprecate the claimed invention. *In re Fritch*, 972 F.2d 1260, 23 USPQ 2d 1780, 1784 (Fed. Cir. 1992).

Thus, Applicants respectfully submit that the Examiner has failed to provide proper motivation for modifying Heeger et al.

Accordingly, Applicants respectfully request reconsideration and withdrawal of

the rejection of Claim 18 under 35 U.S.C. § 103(a) as being unpatentable over Heeger et al.

On page 2 of the outstanding Office Action, the Examiner rejected Claims 18-23, 27, and 28 under 35 U.S.C. § 103(a) as being unpatentable over Heeger et al. in view of Jang et al. ("Dendritic Physical Gel: Hierarchical Self-Organization of a Peptide Core Dendrimer to Form a Micrometer Scale Fibrous Assembly").

Applicants respectfully traverse this rejection of Claim 18.

Applicants' Claim 18 recites:

An organic EL light emitting device comprising an organic EL light emitting layer and an electrode for applying a voltage to the organic EL light emitting layer, wherein the organic EL light emitting layer includes **a hyperbranched polymer layer having hyperbranched macromolecules uniaxially aligned with a degree of alignment of 0.95 or more** and emits polarized light. (emphasis added)

In Section No. 3 on page 3 of Office Action, the Examiner admitted that Heeger et al. does not teach or suggest that the hyperbranched polymers are self-organized. The Examiner alleged that Jang et al. teaches that hyperbranched macromolecules self-assemble by hydrogen bonding and electrostatic interactions and teaches that the hydrogen bonding and the electrostatic interactions of the hyperbranched macromolecules allow the polymer to have a degree of alignment of 0.95 or more. The Examiner also alleged that it would have been obvious to modify the conjugated polymers of Heeger et al. to be self-assembled through hydrogen bonding and electrostatic interactions in order to have the device of Heeger et al. emit polarized light.

Applicants respectfully disagree.

First, as explained above, Applicants respectfully submit that Heeger et al. fails to teach or suggest the features recited in Applicants' Claim 18.

Second, Applicants respectfully submit that Jang et al. fails to teach or suggest anything concerning the degree of alignment and certainly fails to teach or suggest the hydrogen bonding and the electrostatic interactions allow for the hyperbranched polymer of Jang et al. to have a degree of alignment of 0.95 or more as required by Applicants' Claim 18.

Thus, Applicants respectfully submit that Heeger et al. and Jang et al., alone or in combination, fail to teach or suggest the feature of "a hyperbranched polymer layer having hyperbranched macromolecules uniaxially aligned with a degree of alignment of 0.95 or more" as recited in Applicants' Claim 18.

Third, Applicants respectfully submit that the Examiner has failed to provide proper motivation for modifying Heeger et al. in view of Jang et al. The Examiner has failed to provide any evidence that the hyperbranched polymer of Jang et al. has anything to do with the conjugated polymers of Heeger et al. or any evidence that the conjugated polymers of Heeger et al. can be made to self-assemble.

As discussed above with respect to Heeger et al., instead of basing the conclusion of obviousness based upon Heeger et al. and Jang et al. on actual teachings or suggestions of the prior art and the knowledge of one of ordinary skill in the art at the time the invention was made, the Examiner has improperly used Applicants' own invention as a guide. It is impermissible to use the claimed invention as an instruction manual or 'template' to piece together the teachings of the prior art so that the claimed invention is rendered obvious. The Federal Circuit has previously stated that one cannot use hindsight reconstruction to pick and choose among isolated disclosures in the prior art to deprecate the claimed invention. *In re Fritch*, 972 F.2d 1260, 23 USPQ 2d 1780, 1784 (Fed. Cir. 1992).

Thus, Applicants respectfully submit that the Examiner has failed to provide proper motivation for combining Heeger et al. and Jang et al.

Accordingly, Applicants respectfully request reconsideration and withdrawal of the rejection of Claim 18 under 35 U.S.C. § 103(a) as being unpatentable over Heeger et al. in view of Jang et al.

On page 3 of the outstanding Office Action, the Examiner rejected Claims 18, 24, 25, and 29-34 under 35 U.S.C. § 103(a) as being unpatentable over Heeger et al. in view of Jang et al. and further in view of Slater, Jr. et al. (U.S. 2005/0194603).

Applicants respectfully traverse this rejection of Claims 18 and 30.

Applicants' Claim 18 recites:

An organic EL light emitting device comprising an organic EL light

emitting layer and an electrode for applying a voltage to the organic EL light emitting layer, wherein the organic EL light emitting layer includes a **hyperbranched polymer layer having hyperbranched macromolecules uniaxially aligned with a degree of alignment of 0.95 or more** and emits polarized light. (emphasis added)

Applicants' Claim 30 recites:

A method for fabricating an organic EL light emitting device having an organic EL light emitting layer and an electrode for applying a voltage to the organic EL light emitting layer, the organic EL light emitting device emitting polarized light, the method comprising the steps of:

- (a) preparing a substrate having an electrode formed on its principal plane;
- (b) forming a wall structure on the principal plane, the wall structure having a side face roughly perpendicular to the principal plane; and
- (c) providing a material including hyperbranched macromolecules on the principal plane to form the organic EL light emitting layer including a **hyperbranched polymer layer having the hyperbranched macromolecules aligned roughly in parallel with the side face**. (emphasis added)

In the paragraph bridging pages 3 and 4 and the first full paragraph of page 4 of the outstanding Office Action, the Examiner alleged that the combination of Heeger et al. and Jang et al. teaches each of the features recited in Claims 18 and 30, except for the feature of "a wall structure," which is only recited in Claim 30. The Examiner has relied upon Slater, Jr. et al. to allegedly teach this feature.

Applicants respectfully disagree.

With respect to Claim 18, as noted above, Applicants respectfully submit that Heeger et al. and Jang et al., either alone or in combination, fail to teach or suggest each of the features recited in Applicants' Claim 18. Further, Applicants respectfully submit that Slater, Jr. et al. fails to cure the deficiencies in Heeger et al. and Jang et al., for at least the reasons discussed below with respect to Claim 30.

With respect to Claim 30, in the first full paragraph on page 4 of the outstanding Office Action, the Examiner alleged, "Also, the Slater, Jr. [et al.] reference discloses that the barrier layer[, which the Examiner alleged corresponds to wall structure recited in Applicants' Claim 30,] can comprise [a] dendritic structure (see paragraph 0067)."

Claim 30 recites the feature of "a hyperbranched polymer layer having the

hyperbranched macromolecules aligned roughly in parallel with the side face [of the wall structure]." Applicants respectfully submit that Heeger et al., Jang et al., and Slater, Jr. et al., alone or in combination, fail to teach or suggest this feature.

First, the Examiner admitted that the combination of Heeger et al. and Jang et al. fails to teach or suggest the feature of "a wall structure" as recited in Claim 30. Thus, the combination of Heeger et al. and Jang et al. fails to teach or suggest the feature of "a hyperbranched polymer layer having the hyperbranched macromolecules aligned roughly in parallel with the side face [of the wall structure]" as recited in Applicants' Claim 30.

Second, Slater, Jr. et al. also fails to teach or suggest this feature. Slater, Jr. et al. is directed to a device having semiconductor light emitting diodes and fails to even mention polymers. See paragraph no. [0009] of Slater, Jr. et al. Thus, Slater, Jr. et al. clear fails to teach anything concerning a hyperbranched polymer layer having hyperbranched macromolecules as recited in Applicants' Claim 30.

Third, Slater, Jr. et al. mentions, as noted by the Examiner, the term "dendrite" in paragraph no. [0067] of Slater, Jr. et al. However, this portion of Slater, Jr. et al. describes dendrites formed by migrating silver ions, which have absolutely no relation to the hyperbranched macromolecules recited in Applicants' Claim 30. Paragraph no. [0067] of Slater, Jr. et al. states:

In the presence of surface moisture and an electric field, silver ions can form at positive (anodic) metallizations due to oxidation and/or corrosion. When the silver ions migrate to negative (cathodic) metallizations, they can plate out in the form of a dendrite (i.e., a branching structure). The dendrite may eventually bridge the gap between the anode and cathode of the LED and cause a short circuit.

Thus, Heeger et al., Jang et al., and Slater, Jr. et al., alone or in combination, fail to teach or suggest the feature of "a hyperbranched polymer layer having the hyperbranched macromolecules aligned roughly in parallel with the side face [of the wall structure]" as recited in Applicants' Claim 30.

Accordingly, Applicants respectfully request reconsideration and withdrawal of the rejection of Claims 18 and 30 under 35 U.S.C. § 103(a) as being unpatentable over

Heeger et al. in view of Jang et al. and further in view of Slater, Jr. et al.

With respect to new Claim 35, Applicants respectfully submit that the prior art of record fails to teach or suggest the features recited in Claim 35.

Applicants' Claim 35 recites:

An organic EL light emitting device comprising an organic EL light emitting layer and an electrode for applying a voltage to the organic EL light emitting layer; wherein

the organic EL light emitting layer includes a hyperbranched polymer layer having hyperbranched macromolecules uniaxially aligned and emits polarized light;

the organic EL light emitting device further comprises a wall structure having a side face roughly perpendicular to a surface of the hyperbranched polymer layer; and

the hyperbranched macromolecules are aligned roughly in parallel with the side face of the wall structure. (emphasis added)

Similar to Claim 30 discussed above, Applicants respectfully submit that Heeger et al., Jang et al., and Slater, Jr. et al., alone or in combination, fail to teach or suggest the feature of "the hyperbranched macromolecules are aligned roughly in parallel with the side face of the wall structure" as recited in Applicants' Claim 35.

Accordingly, Applicants respectfully submit that the prior art of record, applied alone or in combination, fails to teach or suggest the unique combination and arrangement of elements recited in Claims 18, 30, and 35 of the present application. Claims 19-29, 31-34, and 36-38 depend upon Claims 18, 30, and 35 and are therefore allowable for at least the reasons that Claims 18, 30, and 35 are allowable.

In view of the foregoing amendments and remarks, Applicants respectfully submit that this application is in condition for allowance. Favorable consideration and prompt allowance are solicited.

Application No. 10/500,653
February 13, 2007
Reply to the Office Action dated November 13, 2006
Page 14 of 14

The Commissioner is authorized to charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account No. 50-1353.

Respectfully submitted,

Dated: February 13, 2007

/Peter Medley #56,125/
Attorneys for Applicants

KEATING & BENNETT, LLP
8180 Greensboro Drive, Suite 850
Tyson's Corner, VA 22102
Telephone: (703) 637-1480
Facsimile: (703) 637-1499

Joseph R. Keating
Registration No. 37,368

Peter Medley
Registration No. 56,125



A new hyperbranched polymer with polar chromophores for nonlinear optics

Yadong Zhang*, Tatsuo Wada and Hiroyuki Sasabe

Frontier Research Program, The Institute of Physical and Chemical Research, Hirotsu 2-1, Wako, Saitama 351-01, Japan

(Received 22 April 1996; revised 17 August 1996)

A new three-dimensional hyperbranched polymer with 4-(2-cyano-2-methoxy-carbonylvinyl)aniline as a second-order nonlinear optical chromophore has been synthesized starting from 4-formyl-N,N-di(2-hydroxyethyl)aniline and cyanoacetic acid by a one-pot Knoevenagel polycondensation using 4-(dimethylamino)pyridine as a base. This hyperbranched polymer with a good solubility in polar organic solvents, such as N,N-dimethylformamide and methyl sulfoxide, was characterized by ¹H n.m.r., i.r. and u.v.-vis spectroscopies. Differential scanning calorimeter analysis showed that this polymer exhibited a glass transition temperature at 86°C. The second-harmonic generation signal has been observed from the poled films of this hyperbranched polymer. © 1997 Elsevier Science Ltd.

(Keywords: hyperbranched polymer; one-pot Knoevenagel polycondensation; nonlinear optical materials)

INTRODUCTION

The development of polymers with new chemical structures for nonlinear optical (NLO) materials is an extremely active field. To date, most NLO polymer research has focused on several types of one-dimensional nonlinear optical polymers, such as side-chain polymers (as shown in Figure 1a) and main-chain polymers in which NLO chromophores can be aligned as a shoulder-to-shoulder, a head-to-tail, a head-to-head, and a random style (Figures 1b, c, d, e)¹⁻¹⁰. In order to develop new three-dimensional polymers for nonlinear optics, a hyperbranched polymeric structure was selected as a novel NLO material design. It is well known that hyperbranched polymers with three-dimensional structure are highly branched non-cross-linked polymers synthesized from AB_n monomers where n should be larger than 1. Such materials were first described by Flory¹¹, but only in recent years has purposeful synthesis and characterization of this class of polymers been undertaken¹²⁻²⁰ and attracted increasing attention due to the expectation that their unique spherical structure will impart unusual properties²¹. Recently, hyperbranched polymers and dendrimers with carbazole NLO chromophores have been synthesized in our laboratory²²⁻²⁴. Some of our research work on these materials indicated that such three-dimensional organic NLO materials have good reasonable NLO properties.

We report the synthesis and characterization of a new hyperbranched polyester containing 4-(2-cyano-2-methoxycarbonyl)aniline as a polar NLO chromophore. In this hyperbranched polymer, the chromophores were linked at the cross positions of the branches (as shown in Figure 1f). Each branch chain looks like a head-to-tail main-chain backbone^{3,4,25}.

EXPERIMENTAL

Synthesis of N,N-di(2-acetoxyethyl)aniline (3)

A mixture of 25 g (138 mmol) N,N-di(2-hydroxyethyl)aniline, 50 ml acetic anhydride and 4 ml triethylamine was kept at room temperature for 24 h. To the reaction mixture 300 ml water was added under stirring. After 8 h, the solution was extracted three times with ether, and the ether extract washed three times with 15% Na₂CO₃ and three times with water. After removal of the solvent, N,N-di(2-acetoxyethyl)aniline was obtained in 94% yield (33.2 g) as a colourless oil. ¹H n.m.r. (CDCl₃, TMS, ppm): 2.05 (s, 6H, 2 × -CH₃), 3.62 (t, 4H, J = 6.27 Hz, 2 × -OCH₂-), 4.24 (t, 4H, J = 6.27 Hz, 2 × -NCH₂-), 6.74 (m, 3H, H_{ar}), 7.23 (m, 2H, H_{ar}).

Synthesis of 4-formyl-N,N-di(2-hydroxyethyl)aniline (4)

To 11.4 g (156 mmol) DMF was added 24 g (156 mmol) POCl₃ in 90 min at 0°C. After the reaction mixture warmed to room temperature, 20 g (78 mmol) N,N-di(2-acetoxyethyl)aniline in 50 ml of 1,2-dichloroethane was added. The mixture was refluxed for 6 h and cooled to room temperature. The reaction mixture was added to 500 ml of water. The mixed solution was extracted three times with chloroform. After removal of solvent under reduced pressure, the crude sample was purified by chromatography on a silica gel column to give 18 g (78.8%) of product as colourless oil. ¹H n.m.r. (CDCl₃, TMS, ppm): 2.01 (s, 6H, 2 × -CH₃), 3.69 (t, 4H, J = 6.27 Hz, 2 × -OCH₂-), 4.23 (t, 4H, J = 6.27 Hz, 2 × -NCH₂-), 6.79 (d, 2H, J = 8.91 Hz, H_{ar}), 7.71 (d, 2H, J = 8.91 Hz, H_{ar}), 9.72 (s, 1H, -CHO).

Synthesis of 4-formyl-N,N-di(2-hydroxyethyl)aniline (5)

To 12 g (41 mmol) 4-formyl-N,N-di(2-acetoxyethyl)aniline in 100 ml ethanol was added 8 g (200 mmol) sodium hydroxide in 10 ml water. After reaction was

* To whom correspondence should be addressed

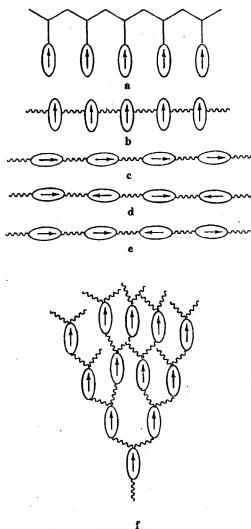


Figure 1 Arrangements of nonlinear optical chromophores in polymeric main chain: (a) side chain; (b) shoulder-to-shoulder; (c) head-to-tail; (d) head-to-head and tail-to-tail; (e) random; (f) hyperbranched

carried out at room temperature for 6 h, 400 ml of water was added. The reaction mixed solution was extracted three times with ethyl acetate. After removal of solvent under reduced pressure, the sample was purified by chromatography on a silica gel column to give 8.7 g of product, which was recrystallized from dichloromethane/hexane. Elemental analysis: calculated for $C_{11}H_{12}NO_2$: C, 63.16; H, 7.18; N, 6.70%. Found: C, 63.28; H, 7.05; N, 6.57%. 1H n.m.r. ($CDCl_3$, TMS, ppm): 3.69 (t, 4H, $J = 5.95$ Hz, $2 \times -OCH_2-$), 3.90 (t, 4H, $J = 5.95$ Hz, $2 \times -NCH_2-$), 3.92 (s, 2H, $2 \times -OH$), 6.69 (d, 2H, $J = 8.91$ Hz, H_{ar}), 7.66 (d, 2H, $J = 8.91$ Hz, H_{ar}), 9.65 (s, 1H, $-CHO$). I.r. (KBr): 3478 (OH), 3032 (aromatic), 2943 (aliphatic), 1685 (C=O), 1608, 1550, 1520 (aromatic), 1404, 1350, 1319, 1248, 1178, 1047, 817 cm^{-1} .

Synthesis of hyperbranched polymer (6)

To 1 g (4.78 mmol) 4-formyl-*N,N*-di(2-hydroxyethyl)aniline and 0.85 g (10 mmol) cyanoacetic acid in 20 ml anhydrous tetrahydrofuran (THF) at 5°C was added 2.1 g (10.2 mmol) *N,N*-dicyclohexylcarbodiimide (DCC). After the reaction mixture was kept at 5°C for 2 h, t.l.c.

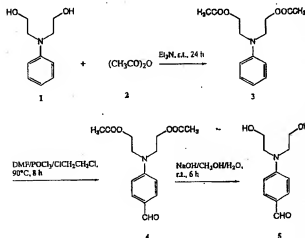
analysis showed that the esterification reaction was finished. The THF solution was then filtered from dicyclohexylurea. To this THF solution at room temperature was added 0.8 g (6.56 mmol) of DMAP. The polycondensation reaction was carried out in THF for 30 min, then organic solvent was removed by a nitrogen purge. The polycondensation was kept in the solid state for 2 h under nitrogen purge. The polymer was dissolved in DMF and purified by reprecipitation into methanol three times from DMF. The polymer prepared was dried under vacuum at room temperature for 48 h; yield 0.87 g. I.r. (KBr): 3033 (aromatic), 2955 (aliphatic), 2216 (CN), 1747 (C=O), 1711 (C=O), 1610, 1570, 1516 (aromatic), 1386, 1331, 1275, 1234, 1178, 1138, 1093, 1005, 933, 825, 760 cm^{-1} .

Measurements

I.r. spectra were recorded on a Shimadzu FTIR-4100 spectrophotometer. U.v.-vis spectra were recorded with a Shimadzu UV-3100 spectrophotometer. 1H n.m.r. spectra were obtained using a J JNM-EX270 spectrometer operating at 270 MHz in $CDCl_3$. Chemical shifts are in parts per million from internal tetramethylsilane. Thermal analysis was conducted on a Perkin-Elmer DSC-7 instrument at a heating rate of $10^\circ\text{C min}^{-1}$. The T_g was taken as the midpoint of the heat capacity change. Thermal gravimetric analyses were performed on a Perkin-Elmer TGA-7 at a heating rate of $10^\circ\text{C min}^{-1}$. The solution viscosity of the polymer was measured on an Ubbelohde viscometer in DMSO solution (0.2 g dl^{-1}) at 30°C . Elemental analyses were performed on a Riken Microanalytical Laboratory.

RESULTS AND DISCUSSION

Schemes 1 and 2 show the synthetic route to hyperbranched polymer 6. *N,N*-Di(2-hydroxyethyl)aniline (1) reacted with acetic anhydride yielded *N,N*-di(2-acetoxyethyl)aniline (3) in the presence of triethylamine. Compound 3 reacted with phosphorus oxychloride ($POCl_3$)/dimethylformamide (DMF) to afford 4-formyl-*N,N*-di(2-acetoxyethyl)aniline (4), which was purified by a column chromatography. 4-Formyl-*N,N*-di(2-hydroxyethyl)aniline (5) could be obtained by the treatment of compound 4 with aqueous NaOH in ethanol. Hyperbranched polymer 6 was synthesized

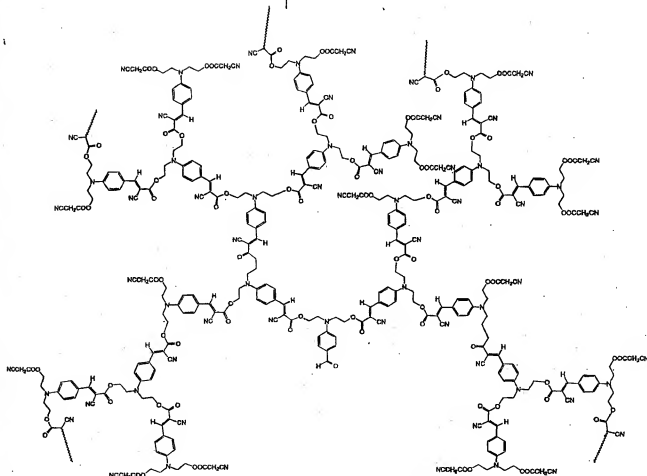


Scheme 1

Scheme 2

from 5 i
condensa
tetrahydra
carbodiim
by thin l
esterifica
pyridine
was remov
was kept
polymer
This h
solid is s
and meth
could be
coating te
spectrum

- 1) $\text{NCCH}_2\text{COOH}/\text{DCC}/\text{CH}_2\text{Cl}_2$
 $> 5^\circ\text{C}$, 2 h
- 2) DMAP, r.t., 2 h



Scheme 2

from **5** in a one-pot reaction by Knoevenagel polycondensation. Esterification of **5** with cyanoacetic acid in tetrahydrofuran (THF) solution using *N,N*-dicylohexylcarbodiimide (DCC) as a water acceptor. After a check by thin layer chromatography (t.l.c.) showed that the esterification reaction was finished, 4-(dimethylamino)pyridine (DMAP) was added as a base. After the THF was removed by a nitrogen purge, the polycondensation was kept in solid state for 2 h to give the hyperbranched polymer **6** in high yield.

This hyperbranched polymer obtained as a yellow solid is soluble in polar organic solvent, such as DMF and methyl sulfoxide (DMSO). Thin films of the polymer could be obtained from its hot DMF solution by a spin-coating technique. Figure 2 shows the u.v.-vis absorption spectrum of the polymer film of about 0.1 μm thickness.

The absorption maximum (λ_{max}) of the chromophore, 4-(2-cyano-2-methoxycarbonylvinyl)aniline, was observed at 405 nm in the u.v.-vis spectrum. However, the absorption due to core terminal group, 4-formylaniline, could not be observed. There is only one core terminal group available in one hyperbranched polymeric molecule. If the molecular weight of the hyperbranched polymer was large, the ratio of the core terminal group would be small. It should be difficult to find the signal of the absorption based on the core terminal group.

Figure 3 shows the ^1H n.m.r. spectrum of the hyperbranched polymer **6**, in which the assignments are generally consistent with the structure drawn. The chemical shifts of the methylene groups in the terminal group ($-\text{NCH}_2\text{CH}_2\text{OOC}-\text{CH}_2\text{CN}$) appear at 4.33 ppm ($-\text{NCH}_2-$), 4.00 ppm ($-\text{CH}_2\text{CN}$) and 3.83 ppm ($-\text{CH}_2\text{O}-$),

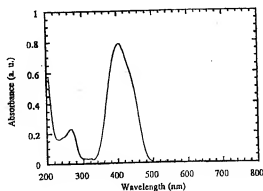


Figure 2 U.V.-vis spectrum of the hyperbranched polymer 6 in thin film

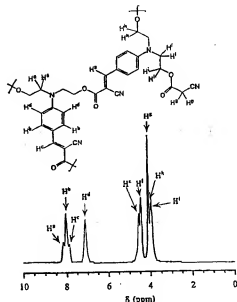


Figure 3 ^1H n.m.r. spectrum of the hyperbranched polymer 6 in DMSO

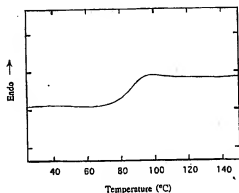


Figure 4 D.s.c. trace of the hyperbranched polymer 6

respectively. The chemical shifts due to the methylene protons of $-\text{NCH}_2\text{CH}_2\text{OOC}(\text{CN})\text{C}=\text{C}$ appear at 4.43 ppm ($-\text{NCH}_2-$) and 3.88 ppm ($-\text{CH}_2\text{O}-$). The chemical shifts of vinyl proton ($-\text{HC}=\text{C}(\text{CN})-$) appear at 7.76 and 8.07 ppm. These two chemical shifts are due to the

existence of two kinds of chromophore conformations. The chemical shift due to formyl group (CHO) of the core terminal group cannot be found in the ^1H n.m.r. spectrum. This result also suggests that the ratio of the core terminal group is very small in this hyperbranched polymer. The assignments of all chemical shifts according to the expected structure are indicated in Figure 3.

The i.r. spectrum of the hyperbranched polymer 6 shows absorption due to a cyano group which can be observed at around 2216 cm^{-1} . Absorption for two kinds of the carbonyl groups appear at 1747 and 1711 cm^{-1} , respectively.

Differential scanning calorimeter (d.s.c.) measurement showed no crystalline transitions for this hyperbranched polymer. Figure 4 shows a d.s.c. trace of the polymer from which the glass transition temperature (T_g) can be deduced. It is found that the T_g of the hyperbranched polymer 6 is about 86°C . Thermal stability of the hyperbranched polymer 6 was studied by thermal gravimetric analysis (t.g.a.). The hyperbranched polymer appears to be stable in air up to a temperature of about 330°C .

The viscosity ($\eta_{\text{inh}} = 0.27\text{ dl g}^{-1}$) of the hyperbranched polymer 6 was obtained from DMSO solution at 30°C . According to work on the relationship between the viscosity η and the molecular weight of the hyperbranched polyesters reported by Turner *et al.*²⁸, the molecular weight for hyperbranched polyesters with $\eta_{\text{inh}} = 0.27\text{ dl g}^{-1}$ ranges from 10 000 to 100 000. Although a direct comparison of the viscosity of the hyperbranched polymer 6 with that of hyperbranched polyester is not strictly valid, a comparison of their physical properties is reasonable. The value of this viscosity suggests that the molecular weight of the hyperbranched polymer 6 should be large.

The orientation of chromophores in the polymeric thin films monitored by second harmonic generation (s.h.g.) could be achieved by the corona poling (7.5 kV) at about 120°C . The s.h.g. measurements were performed using a polarized Q-switched Nd-YAG laser beam ($\lambda = 1064\text{ nm}$). A Y-cut quartz crystal plate was used as a reference. The second harmonic (s.h.) intensity was measured using the standard Maker fringe technique²⁹. The s.h.g. signal was observed from these poled films of the hyperbranched polymer 6. However, the s.h. coefficient (d_{31}) was not large. This was probably caused by the difficulty in alignment of the NLO chromophores which are at the cross positions of the

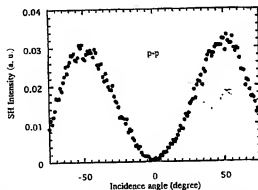


Figure 5 S.h. intensity vs incidence angle for a poled film of the hyperbranched polymer 6 with $0.23\text{ }\mu\text{m}$ thickness

branches, like the head-to-tail polymers²⁸. In this hyperbranched polymer, each branch chain looks like a head-to-tail main-chain. Poling behaviour of this type of hyperbranched polymer should be similar to the head-to-tail polymer. The d_{33} could be estimated from the angular dependence of the s.h. intensity using the formula given by Hayden²⁹. Figure 5 shows a typical relation between the s.h. intensity and the incidence angle. A Y-cut quartz plate ($d_{11} = 0.5 \text{ pmV}^{-1}$) was used as a reference material. Preliminary results of the s.h.g. studies indicated that the value of d_{33} for the hyperbranched polymer 6 was about 2.8 pmV^{-1} . Further studies and results on the synthesis and nonlinear optical properties of the hyperbranched polymers with NLO chromophores at side position of the branches will be forthcoming.

CONCLUSIONS

A hyperbranched polymer containing a polar chromophore, 4-(2-cyano-2-methoxycarbonyl(vinyl)aniline, has been synthesized in a one-pot reaction from 4-formyl-N,N-di(2-hydroxyethyl)aniline by Knoevenagel polycondensation using DMAP as a base catalyst. The spectroscopies of the polymers were in good agreement with the proposed structure. Detailed studies on the NLO properties of this type of polymer are now underway.

REFERENCES

1. Winoto, D. and Carr, S. H., *Polymer*, 1995, 36, 4561.
2. Choi, D. H., Wijekoorn, W. M. K., Kim, H. M. and Prasad, P. N., *Chem. Mater.*, 1994, 6, 234.
3. Fuso, F., Padias, A. B. and Hall, H. K., Jr., *Macromolecules*, 1991, 24, 1710.
4. Stenger-Smith, J. D., Fischer, J. W., Henry, R. A., Hoover, J. M., Nedler, M. P., Nissan, R. A. and Lindsay, G. A., *J. Polym. Sci., Part A: Polym. Chem.*, 1991, 29, 163.

5. Stenger-Smith, J. D., Henry, R. A., Hoover, J. M., Lindsay, G. A., Nadler, M. P. and Nissan, R. A., *J. Polym. Sci., Part A: Polym. Chem.*, 1993, 31, 2899.
6. Wright, M. E. and Mullick, S., *Macromolecules*, 1992, 25, 6045.
7. Zentel, R., Baumann, H. and Scharf, D., *Makromol. Chem., Rapid Commun.*, 1993, 14, 124.
8. Xu, C., Wu, B., Becker, M. W., Dalton, L. R., Ranon, P. M., Shi, Y. and Steier, W. H., *Chem. Mater.*, 1993, 5, 1439.
9. Xu, C., Wu, B. and Dalton, L. R., *Macromolecules*, 1992, 25, 6716.
10. Turner, S. R., Walter, F., Voit, B. I. and Mourey, T. H., *Macromolecules*, 1994, 27, 1611.
11. Flory, P. J., *J. Am. Chem. Soc.*, 1952, 74, 2718.
12. Gaynor, S. G., Edelman, S. and Matyjaszewski, K., *Macromolecules*, 1996, 29, 1079.
13. Jikei, M., Hu, Z., Kakimoto, M. A. and Imai, Y., *Macromolecules*, 1996, 29, 1062.
14. Kim, Y. H. and Webster, O. W., *Macromolecules*, 1992, 25, 5561.
15. Hawker, C. J. and Frechet, J. M. J., *J. Am. Chem. Soc.*, 1991, 113, 4583.
16. Miller, T. M., Neenan, T. X., Kwock, E. W. and Stein, S. M., *J. Am. Chem. Soc.*, 1993, 115, 356.
17. Kricheldorf, H. R., Zang, Q. Z. and Schwarz, G., *Polymer*, 1982, 23, 1821.
18. Kim, Y. H., *J. Am. Chem. Soc.* 1992, 114, 4947.
19. Malmstrom, E., Johansson, M. and Hult, A., *Macromolecules*, 1995, 28, 1698.
20. Kricheldorf, H. R., Stober, O. and Lubbers, D., *Macromol. Chem. Phys.*, 1995, 196, 3549.
21. Tomalia, D. A., Naylor, A. M. and Goddard, W. A., III., *Angew. Chem., Int. Ed. Engl.* 1990, 29, 138.
22. Zhang, Y. D., Wang, L., Wada, T. and Sasabe, H., *Macromol. Chem. Phys.*, 1996, 197, 667.
23. Zhang, Y. D., Wang, L., Wada, T. and Sasabe, H., *J. Polym. Sci., Part A: Polym. Chem.*, 1996, 34, 1359.
24. Wada, T., Wang, L., Zhang, Y. D., Tain, M. and Sasabe, H., *Nonlinear Optics*, 1996, 15, 103.
25. Mitchell, M. A., Tomida, M., Padias, A. B. and Hall, H. K., Jr., *Chem. Mater.*, 1993, 5, 1044.
26. Turner, S. R., Walter, F., Voit, B. I. and Mourey, T. H., *Macromolecules*, 1994, 27, 1611.
27. Jerphagnon, J. and Kurtz, S. K., *J. Appl. Phys.*, 1970, 41, 1667.
28. Zentel, R., Baumann, H. and Scharf, D., *Makromol. Chem., Rapid Commun.*, 1993, 14, 124.
29. Hayden, L., Sauter, G. F., Ore, F. R., Pasillas, P. L., Hoover, J. M., Lindsay, G. A. and Henry, R. A., *J. Appl. Phys.*, 1990, 68, 456.

also shown that reduction in water or formamide solution with dithionite produces dendrimeric poly(anion radicals) in which each diimide group had taken up one electron. The reduced dendrimers were characterized by optical spectroscopy, electrochemistry, and ESR. Importantly, the anion radical moieties are stable in these solvents in the absence of oxygen. In degassed formamide stability is complete even at 120 °C for several hours.

To our knowledge the only other study of conducting dendrimers is one in which dendritic polystyeres were prepared with two, four, or eight TTF units.⁹ Conductive charge transfer salts with $\sigma = 2 \times 10^{-3}$ S/cm were precipitated as powders by addition of TCNQ.

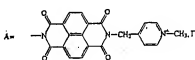
The present study provides thin film materials with humidity dependent conductivities as high as 18 S/cm. This value is the highest reported for an air-stable n-doped polymer. Previously examples of air-unstable n-doped polymers are polyacetylene reduced with sodium naphthalide (film, $\sigma = 80$ S/cm),¹⁰ polypyridine reduced with sodium naphthalide (powder, $\sigma = 0.1$ S/cm),¹¹ and a film of electrochemically polymerized, cathodically reduced dithienylvinylene (bathed in acetonitrile, tetraethylammonium perchlorate solution, $\sigma = 2$ S/cm).¹²

Results

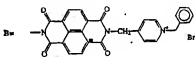
Ammonia core, poly(amidoamine) (PAMAM) dendrimers, generations 1–5, were modified with diimide A yielding D-A

D = generation 1–5 PAMAM dendrimers, NH₂ Core.

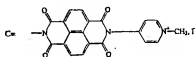
D—A



D—B

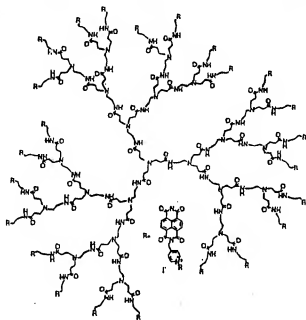


D—C



as previously reported.⁸ The generation-3 dendrimer (D3), which is terminated with 24 amine groups, was modified with three different diimide groups, yielding D3-A, D3-B, and D3-C. Diaminoethane-core, generation-3 PAMAM (36 terminal amines) was similarly modified producing D3-A.

Initial attempts to cast films utilized the dendrimers D-A in aqueous solution, reduced with 1.1 equiv of sodium dithionite. Using various temperatures and concentrations it proved impossible to form homogeneous and coherent films. The precipitated powders formed by evaporation of water at room temperature under flowing argon were, however, collected and pressed into pellets. Four probe conductivity measurements were performed



D3-A

at room temperature. The conductivity of D1-A was below 10^{-7} S/cm. D2-A gave $\sigma = 1 \times 10^{-4}$ S/cm. The conductivities of D3-A, D4-A, and D5-A were about 7×10^{-4} S/cm.

In a search for a polar solvent more suitable for film casting, formamide was discovered to have useful properties. The reduced dendrimers are more soluble and the diimide anion radicals attached to the dendrimers aggregated into π -dimers and π -stacks in this solvent.⁸ D3-A exhibited better solubility and better film forming properties than other D-A generations and it was chosen for extensive study. An apparatus appropriate for casting films from formamide was constructed, which allowed control of the temperature and kept the sample under flowing argon during film casting. The dendrimers, reduced with 1.1 equiv of sodium dithionite, gave dark brown films on glass slides. These films were rather brittle and were not removed from the glass.

Optical spectra were recorded for D3-A films.³ Films cast at 120 °C showed an intense NIR peak at 1140 nm, assigned from previous studies to a π -dimer of two anion radicals coming together face-to-face.⁶ Casting at 60 °C gave rise to a 2300-nm absorption with a weaker π -dimer peak. The longer wavelength absorption is characteristic of excitation of conduction electrons along π -stacks.^{6,13} When 0.5 equiv of dithionite (0.55 e/imide) was used for reduction, the π -dimer peak was even weaker and the π -stack absorption was shifted to the IR region with maximum at 3000 nm. The IR spectra also showed imide carbonyl bands at 1640 and 1527 cm^{-1} . These are typical for naphthalene diimide anion radicals.⁶ The bands are shifted compared to the neutral diimide, which has carbonyl bands at 1716 and 1670 cm^{-1} . Visible spectra of these films showed a peak at 450 nm, consistent with previous solution studies on these compounds and other imide derivatives.⁶

D3-B films were cast from formamide at 60 °C. The solubility of both neutral and reduced forms of D3-B is better than for D3-A and this resulted in more homogeneous films. Films formed on a silicon-coated paper substrate could be bent 30° above or below the film plane without any noticeable crack

- (9) Bryce, M. R.; Devonport, W. *Synth. Met.* 1996, 76, 305.
- (10) Chiang, C. K.; Drury, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H. *J. Am. Chem. Soc.* 1978, 100, 1013.
- (11) Yamamoto, T.; Maruyama, T.; Zhou, Z.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikada, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota K. *J. Am. Chem. Soc.* 1994, 116, 4832.
- (12) Zotti, G.; Schiavon, G. *Synth. Met.* 1994, 63, 53.

- (13) Torrance, J. B.; Scott, B.; Welber, B.; Kaufman, F. D.; Seiden, P. E. *Phys. Rev. D* 1979, 19, 730.

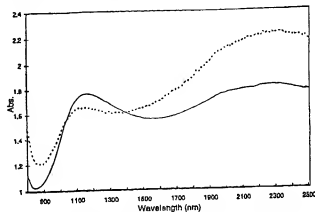


Figure 1. NIR of D3-B films cast at 60°C: 1.1 e/mide reduced (solid line) and 0.55 e/mide (dashed line).

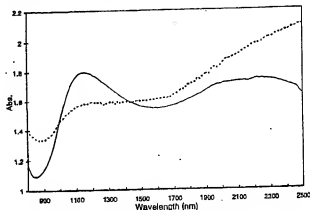


Figure 2. NIR of D3-A films cast at 60°C: 1.1 e/mide reduced (solid line) and 0.55 e/mide (dashed line).

lines, and using a sharp blade, films could be removed from the substrate providing flexible, freestanding films. Fully reduced films showed NIR peaks at 1140 and 2200 nm (Figure 1). Using 0.55 e/mide, half-reduced films showed a small peak at 1140 nm and major absorption at 2200 nm.

D3-C was of interest because when reduced, it showed somewhat longer NIR absorption in solution. Unfortunately, it precipitated too rapidly upon reduction in formamide and we were not able to cast films. A NIR spectrum of the solid was measured by coating the powder onto a glass slide. A fully reduced sample showed a small peak at 1140 nm, while in a half-reduced sample, the 1140-nm peak has completely disappeared in favor of a longer wavelength (>2200 nm) band. Pressed powder conductivities were 4×10^{-3} and 6×10^{-2} S/cm for fully reduced and half-reduced samples, respectively, slightly higher than for powders of D-A.

D3-A films (ethylenediamine core) were similarly cast at 60°C from formamide. NIR on fully reduced films showed a peak at 1140 nm and a relatively large absorption peak at 2300 nm extending into the IR region (Figure 2). For half-reduced films, the 1140-nm peak appears as a shoulder in the spectrum with the main absorption peak at 3000 nm.

Four-probe conductivity measurements were made on D3-A, D3-B, and D3-C films at about 25% relative humidity (RH) at room temperature (Table 1). The in-plane conductivities were generally higher for films cast at 60°C, not 120°C, and for films reduced with 0.55 e/mide, not 1.1 e/mide. The values ranged from 2×10^{-3} to 5×10^{-2} S/cm. The conductivities were ohmic, and there was no evidence for depletion or polarization when current was passed for several hours and then

Table 1. Dendrimer Films Conductivity (S/cm)

	1.1 e/mide 25% RH	0.5 e/mide 25% RH	1.1 e/mide 90% RH	0.5 e/mide 90% RH
D3-A	1.2×10^{-3}	4.7×10^{-3}	0.12	11
D3-B	1.7×10^{-3}	5.0×10^{-2}	0.08	15
D3-C	1.9×10^{-3}	4.2×10^{-2}	0.11	18

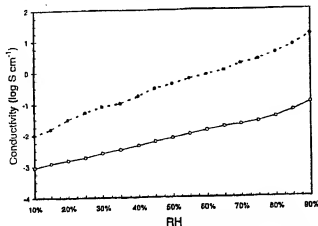


Figure 3. Conductivity vs. relative humidity of D3-B films: 1.1 e/mide reduced (solid line) and 0.55 e/mide (dashed line).

switched. The values were stable for samples stored in air for several weeks. Conductivity for a sample film placed between two glass plates and sealed with epoxy was stable for several months: Two probes were used to measure in-plane and cross-plane conductivities across the same distance and gave identical values. Alternatively two-probe, across-the-film measurements were compared to four-probe measurements along the film, which were corrected for the contact resistance. Again, the values were the same indicating isotropic conductivity.

Films of D3-A, D3-B, and D3-C exhibited enhanced conductivity when placed in a humid atmosphere. Using controlled humidity argon the change was shown to be reversible and about two orders of magnitude between 10 and 90% (RH). At 90% RH, fully reduced D3-A, D3-B, and D3-C have conductivity values (Table 1) of about 0.1 S/cm. Half-reduced samples have conductivities of about 10 S/cm. At 100% RH (rain), a half-reduced D3-B film showed $\sigma = 25$ S/cm. The conductivity was always ohmic and no evidence for polarization was observed even at extreme humidity levels. The values are repeatable (within 2%) through several 10–90% RH reversible cycles before the films develop crack lines. After that, conductivity drops dramatically. Plots of conductivity vs RH (Figure 3) reveal that between 15 and 65% RH the conductivity increase is almost linear with changes of less than one order of magnitude. A more rapid change is observed above 65% RH. In all our tests, conductivities responded quickly to changes in humidity (Figure 4). Specifically, it took less than 5 min for the conductivity to reach its steady state value when RH was increased from 30% to 40% RH.

In order to assess the effect of humidity on structure, one side of a 1-cm quartz cell was coated with a D3-A film. A NIR spectrum was taken after the closed cell was dried and held under argon for 24 h. Another NIR was taken after the cell was filled with water-saturated argon for 2 h. The base line of the wet film shifted up about 10% but there was no change in the shape of the spectrum.

A wide-angle X-ray diffraction instrument was fitted with a homemade device to control the humidity above the sample being analyzed. Data were recorded on both dry and wet films.

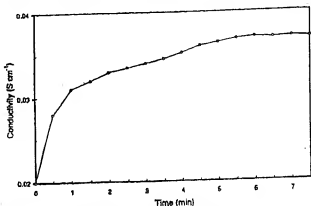


Figure 4. Conductivity vs time for D3-B. Relative humidity stepped from 30% to 40% at $t = 0$.

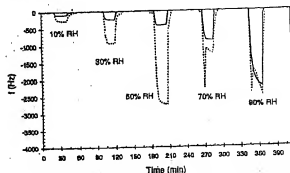


Figure 5. D3-A films QCM frequency response to relative humidity: neutral (solid line); reduced (dashed line).

In both cases, the films gave only a broad peak corresponding to expectations for an amorphous film without crystalline structure.

The quartz crystal microbalance was used to study film hydration. D3-A and D3-B in both neutral and reduced forms were coated on calibrated 9-MHz quartz crystals. Samples were mounted in a stainless steel box. The humidity was varied between 10 and 90% in 10% increments. Twenty minutes were given to each humidity level to allow the film to reach equilibrium. Another 20 min of purging with dry nitrogen allowed films to dehydrate. After dehydration they were brought up to the next humidity level. Consider first the data (Figure 5) for unreduced D3-A and D3-B. Change in the RH led to a rapid decrease in the frequency due to the absorption of water by the film, then a relatively constant frequency indicating equilibration was complete. After each dehydration the frequency returned to its original value. Using the Sauerbrey equation¹⁴ the weight of the absorbed water was calculated from the frequency. In Figure 6 the weight is plotted as a function of RH. Above 60% RH the weight of water increases rapidly, reaching 37% and 47% of the dry film weight at 90% RH for D3-A and D3-B, respectively.

The reduced films behave the same up to 60% RH except that, comparing the same initial weight of film, the reduced films take up more water. For example, at 50% RH unreduced D3-A takes up 10% of its original weight, and reduced D3-A takes up 26%. Above 60% RH the experimental curves for the reduced dendrimers (Figure 5) are irregular. When the humidity is turned on, the frequency decreases as expected, then rises and drops again as time passes. Clearly, major changes in the film structure are occurring and one cannot use these data to weigh the absorbed water.

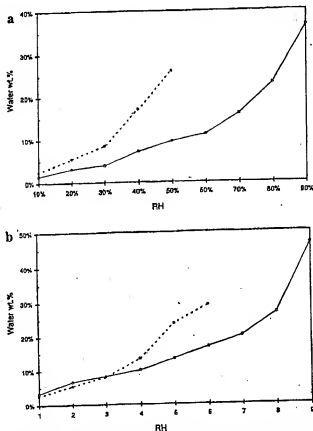


Figure 6. Weight percent water in films held at different relative humidity: neutral (solid line), reduced (dashed line); (a) D3-A, (b) D3-B.

Discussion

These films constitute the first examples of electrically conducting dendrimers and one of the few examples of dendrimers used for materials chemistry. The results are interesting in the context of dendrimer structure and in the context of conducting polymers. As noted above, *n*-doped conducting polymers are not air stable and only a few reliable conductivity values have been reported. The values, >10 S/cm, reported here for hydrated, mixed valence films are reasonably high and suggest that further structural development may give conductivities as high as more traditional oxidized (*p*-doped) conjugated polymers like polythiophenes or poly(phenylenevinylene). In terms of structure and morphology the dendrimer films are, of course, quite different from typical conducting polymers, which have long conjugated chains and improved conductivity for oriented, partially crystalline samples. Dendrimer films rely on π -stack interactions, they are amorphous, and improved conductivity is achieved by hydration, a process which seems (see below) to involve plasticization. Therefore, in addition to their intrinsic importance these new materials introduce some new perspectives on conducting materials.

On the negative side we found it difficult to form high-quality thin films. Even with the good fortune of developing formamide as a casting solvent only a few of the dendrimers gave good films. In only one case, D3-B, could a reduced film be used as a free-standing film: This poor film-forming quality results, in part, because the modified, reduced dendrimers are salts, and, perhaps in part, because there is little interpenetration of the chains of neighboring dendrimer molecules. It should be quite feasible, of course, to use other modifying groups and other dendrimer structures to improve on this situation.

Electrically Conducting Dendrimers

Insight into the structure and conductivity of these materials can be best made by comparison with other diimide anion radical conductors.^{4,7} Previous studies of reduced diimides as pure salts, as salts imbedded in PVA, or as electroprecipitated diimide/polyacetylene films demonstrated that the conducting films contained π -stacks of anion radicals oriented in the film plane. This was reflected in the anisotropy of the conductivity and NIR spectra. Here also the data demonstrate a relationship between structure, NIR spectra, and conductivity. All the conducting films had very long wavelength absorption bands in the NIR/IR. These bands are characteristic of conductors and in this case the wavelength is qualitatively characteristic of the delocalization length along π -stacks. Comparison of dendrimer films with the other diimide anion radical films demonstrates that covalent attachment of the anion radicals to the dendrimer scaffold did not inhibit stack formation.

On a larger scale the relatively high conductivity values demand that these stacks be organized into a conducting network. This requires interaction between the diimides on neighboring dendrimer molecules. Since the conductivity values for the dry dendrimer films are as high as those for pure diimide anion radical films, it indicates that this intermolecular interaction and network formation is effective even though much of the mass is PAMAM, not conductor. In contrast to films formed using small diimide molecules these films are isotropic in their structure and conductivity. It means that the 3-dimensional structure of the dendrimer led to a 3-dimensional network.

The relationship between structure, NIR spectra, and conductivity is also demonstrated for partially reduced films. In solution no evidence has been found for mixed valence (neutral plus anion radical) stacks. In these films, however, partially reduced films show increased NIR/IR absorbance (more intense and longer wavelength) and higher electrical conductivity. Higher conductivity for mixed-valence π -stack materials is commonly observed and theoretically predicted.⁴ Indeed, we cannot rule out the possibility that even in our "fully reduced" materials, there are some neutral diimide moieties which contribute to formation of highly reduced, but mixed stacks.

The humidity/conductivity phenomenon is of obvious interest because the effect on conductivity is quite large and because we believe these are electronic, not ionic conductors. The measurements reported above demonstrate that the films hydrate rapidly and reversibly and this absorption of water is responsible for the increased conductivity. This hydration would be expected to enhance ionic conductivity and, although some ionic conductivity cannot be ruled out, we find no evidence for this effect. It is not probable that ionic conductivity would be high enough to contribute significantly with the high levels of electronic conductivity. Since the dendrimer is so large, inorganic ions, sodium or iodide, associated with the reduced dendrimer as counterions are the species most likely to carry ionic current. If they do migrate, the concentrations of these ions would become polarized, and depleted by electrolysis at the electrodes, and show the usual effects of ionic conductivity. These are not observed. It is postulated, therefore, that absorbed water somehow improves the electronic conductivity. Since the NIR spectra do not change very much with hydration and there is no evidence for crystallization in the hydrated films, we conclude that the water enhances charge transport between stacks in this amorphous material.

The quartz crystal microbalance measurements are extremely interesting in this regard. The data on unhydrated films show that considerable amounts of water are absorbed. It is known that the PAMAM core is hydrophilic, but the pyridinium iodide salt moieties can be involved in this phenomenon as well. The

reduced films take up even more water, presumably because they are more ionic. In the low RH range, the films appear to be sufficiently rigid so that the Sauerbrey equation¹⁴ can be used to estimate the water uptake, but at high humidity the QCM measurements indicate that a more complicated phenomenon is occurring. It is easy to observe that the films become much less brittle and somewhat sticky when the room humidity is high and it seems likely that hydration plasticizes the materials leading to a viscoelastic film. It is known that such a material does not respond to the vibration of the quartz crystal as a rigid body.^{14,15} The experimental observations (Figure 5) can then be explained as follows. When the humidity is turned on the QCM frequency decreases as water is absorbed, but sufficient water leads to a phase change to the viscoelastic phase. This loss of rigidity causes the frequency to increase, followed eventually by a further frequency decrease due to the absorption of more water.

It is this new, viscoelastic phase that leads to the highest conductivity values for both fully reduced and partially reduced films. The correlation of the change in phase with the change in conductivity above 60% suggests that the phase change is responsible for the conductivity change. Since there is no evidence that hydrated films have different stack structures we suggest that the increase in conductivity results from the increased mobility of stacks in the highly hydrated films. Many studies of redox polymers which conduct by electron (and counter ion) hopping from one redox site to a neighboring site have shown that solvating the polymer film increases the hopping rate and it has been suggested that the mobility of the species in the polymer is important in this phenomenon. It could of course be true that the barrier to inter-stack hopping could also be lowered by solvation of the ions involved.

Our results are interesting in the field of conducting polymers because conjugated chain conducting polymers usually give higher conductivity from more organization.¹⁶ One interesting example of the effects of solvation on conductivity has been reported by Murray and co-workers for films of the ladder polymer poly(benzimidazobenzophenanthroline).¹⁷ As a dry film this polymer has electronic conductivity of 0.2 S/cm. Wetted with acetonitrile the conductivity is ionic and smaller (10^{-3} – 10^{-2} S/cm). This counter example shows that swelling of a conducting polymer film with solvent can actually decrease the electronic conductivity to a level at which ionic conduction dominates.

Increased conductivity from increased humidity was previously reported for polyaniline and for a black powder obtained from the anodic oxidation of thionaphtheneindole.¹⁸ In the latter case it was shown that the conductivity increased from about 10^{-2} to 7×10^{-4} S/cm at 85% RH. The majority of the conductivity increase occurred between 40% and 80% RH. The time response of these powders was on the order of ten hours, much slower than the dendrimer films, which have a response time comparable to a commercial PACER hygrometer.

Finally, we turn to the dependence of conductivity on structure. For the set D-A, D-B, D-C, all stacked similarly and gave similar conductivities. Although we thought that the larger dendrimers might force the diimide groups into closer proximity, there is also little difference between the packed powder

(15) Grate, J. W.; Martin, S. J.; White, R. M. *Anal. Chem.* 1993, 65, 940A.

(16) *Conjugated Polymers*; Bredas, J. L.; Silbey, R., Eds.; Kluwer: Dordrecht, The Netherlands, 1991. *Conjugated Polymers and Related Materials*; Salbeck, W. R.; Lundström, L.; Rånby, B., Eds.; Oxford University Press: Oxford, 1993.

(17) Wilcoxon, K.; Murray, R. W. *J. Phys. Chem.* 1988, 92, 3642.

(18) Campor, M.; Casalbore-Miceli, G.; Camaioni, N.; Chiodelli, G. *Synth. Met.* 1995, 73, 131.

conductivities of D2-A—D5-A. D1-A, which has only 6 diimide groups, is a much worse conductor, but the 96 diimides on D5-A offer no advantage compared to the 12 on D2-A. We postulate that only short π -stacks are formed on any dendrimer, so the conducting network is similar for all the cases studied. It is clearly true on the other hand that there is sufficient flexibility in the PAMAM core to allow π -stack interactions both intra- and intermolecularly.

In conclusion we have developed the first examples of a new class of conducting polymers. The structure and conductivity can be understood to a certain extent in terms of π -stacks, the 3-dimensional nature of dendrimers, and the hygroscopic nature of the material. A number of interesting experiments are envisaged in future work.

Experimental Section

Materials. The syntheses of the modified dendrimers have been reported elsewhere.¹ Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) was used without further purification. UV studies showed that a 10% excess was needed to ensure complete reduction.

Film Casting. A digital controlled temperature hot plate (Mirak Thermolyne) was used for film casting. A microslide (Clay Adams gold seal cover glass) which provided the film-forming surface was placed onto a glass plate. The glass plate was covered with a glass bell jar and sealed with vacuum grease. The top opening of the bell jar was closed with a rubber septum. Two needles allowing a flow of high purified argon were inserted through the rubber septum into the bell jar. A gas trap was connected to the side arm of the bell jar to monitor. Film casting temperature was varied by changing the temperature of the hot plate placed directly under the bell jar.

Solutions of modified dendrimer (10 wt %) were prepared by dissolving the proper amount of compound in formamide (Aldrich Chemicals, 99+% grade). The solution was heated at the casting

temperature and was purged with argon to remove oxygen. In another vial, a weighed amount of sodium dithionite was prepared. The vial was closed with a rubber septum and deoxygenated with argon. The solution was first added into the vial with an air-tight syringe for reduction, and then transferred onto the microslide. Depending on the casting temperature, 2 to 6 h were required to form a dark brown colored film with a thickness of 3 to 5 μm . For samples that do not form films, the dried powder was collected from the glass slides and pressed into a pellet for further studies.

Vis and NIR spectra were taken directly on the films formed on the microslides. A reference spectrum with just the microslide was obtained to correct the base line. All of the Vis and NIR data were collected with a computer-controlled Cary 17 spectrometer at room temperature. Samples for IR measurements were prepared by coating the films onto a slice of silicon wafer.

Conductivity measurements were performed with a standard 4-probe method. Four silver wires (Ted Peller) were parallel attached to the surface of the sample with silver paste. The sample was held in a bell jar equipped with a PACER hygrothermometer model DH200/300 humidity sensor. One stream of argon is allowed to pass through a distilled water bath and then combined with a stream of dry argon before introduction into the bell jar. The humidity was controlled by varying the ratio of the two argon streams. To record the conductivity number at a specific humidity, the humidity was maintained for 5 min before the conductivity reading was recorded.

Acknowledgment. Assistance from Toshihiro Hashimoto, Ibro Tabakovic, and Jun Han is acknowledged. The QCM experiments were performed at Iowa State University with the assistance of Marc Porter and Chuan Jian Zhong. This work was supported by the National Science Foundation and the Army Research Laboratory/Michigan Molecular Institute, Dendritic Polymer Research Center, Contract No. DAAN01-96-2-0044.

JA963270I